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Methods for the Determination of Inorganic Compounds in Drinking Water. Methods 300.0 and 200.8

(U.S.) Environmental Monitoring Systems Lab., Cincinnati, OH

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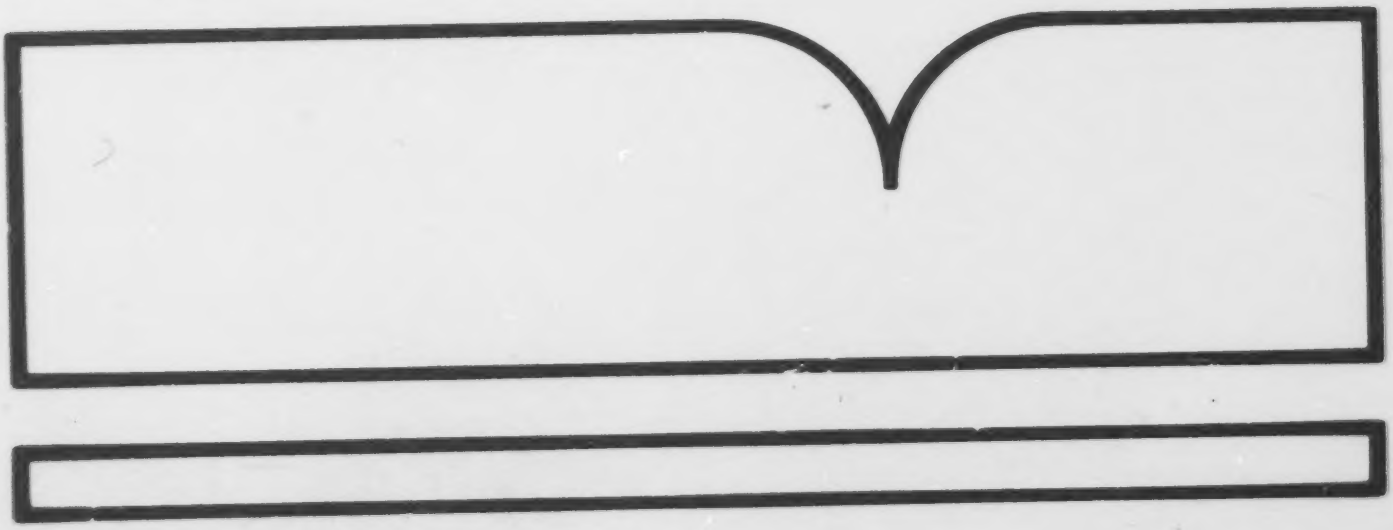

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Abstract: Contents: EPA method 200.8 Determination of Trace Elements in Water and Waste by Inductively Coupled Plasma/Mass Spectrometry; EPA method 300.0 Determination of Inorganic Anions by Ion Chromatography.

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METHODS FOR THE DETERMINATION OF INORGANIC COMPOUNDS IN DRINKING WATER

METHODS 300.0 AND 200.8

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
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Table of Contents:

EPA/method
1. 200.8 Determination of Trace Elements in Water and waste by Inductively Coupled Plasma/Mass Spectrometry, pages 1-44

EPA method
2. 300.0 Determionation of Inorganic Anions by Ion Chromatography, pages 1-20

Method 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

VERSION 4.0

September 1989

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INDEX

Section Number	Subject	Page
1	Scope and Application	1
2	Summary of Method	2
3	Definitions	2
4	Interferences	4
5	Safety	6
6	Apparatus and Equipment	6
7	Reagents and Consumable Materials	8
8	Sample Collection, Preservation and Storage	13
9	Calibration and Standardization	14
10	Quality Control	16
11	Procedure	19
12	Calculations	21
13	Precision and Accuracy	22
14	References	23

TABLES

1. Estimated Instrument Detection Limits, Method 200.8
2. Common Molecular Ion Interferences in ICP-MS.
3. Internal Standards and Limitations of Use.
4. Recommended Analytical Isotopes and Additional Masses which Must be Monitored.
5. Recommended Elemental Equations for Data Calculations.
6. Instrument Operating Conditions for Precision and Accuracy Data.
7. Total Recoverable Method Detection Limits.
8. Precision and Recovery Data in Aqueous Matrices.
9. Precision and Recovery Data in Solid Matrices.

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NOTICE

This method has been peer and administratively reviewed by the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

METHOD 200.8 - DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of dissolved elements in ground waters, surface waters and drinking water supplies. It may also be used for the determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and solid waste samples.

1.2 Dissolved elements are determined after suitable filtration and acid preservation. Acid digestion procedures are required prior to the determination of total recoverable elements. In order to reduce potential interferences, the dissolved solids level should not exceed 0.2% (w/v), see 4.1.4.

1.3 This method is applicable to the following elements:

Element		Chemical Abstract Services Registry Numbers (CAS RN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

Estimated instrument detection limits for these elements are listed in Table 1. These are intended as a guide to instrumental limits typical of a system optimized for multi-element determinations and employing commercial instrumentation and

pneumatic nebulization sample introduction. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

1.4 This method should be used by analysts experienced in the use of inductively coupled plasma - mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of six months experience with commercial instrumentation is recommended.

2. SUMMARY OF METHOD

2.1 The method describes the multi-element determination of trace elements by ICP-MS[1-3]. Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique (section 4) must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standardization.

3. DEFINITIONS

3.1 DISSOLVED - Material that will pass through a 0.45 µm membrane filter assembly, prior to sample acidification.

3.2 TOTAL RECOVERABLE - The concentration of analyte determined on an unfiltered sample following treatment with hot dilute mineral acid.

3.3 INSTRUMENT DETECTION LIMIT (IDL) - The concentration equivalent of the analyte signal, which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).

3.4 METHOD DETECTION LIMIT (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

3.5 LINEAR DYNAMIC RANGE (LDR) - The concentration range over which the analytical working curve remains linear.

3.6 LABORATORY REAGENT BLANK (LRB) (preparation blank) - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

3.7 CALIBRATION BLANK - A volume of ASTM type I water acidified with the same acid matrix as is present in the calibration standards.

3.8 INTERNAL STANDARD - Pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.9 STOCK STANDARD SOLUTION - A concentrated solution containing one or more analytes prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.

3.10 CALIBRATION STANDARD (CAL) - A solution prepared from the stock standard solution(s) which is used to calibrate the instrument response with respect to analyte concentration.

3.11 TUNING SOLUTION - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

3.12 LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is within accepted control limits.

3.13 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for the concentrations found.

3.14 QUALITY CONTROL SAMPLE (QCS) - A solution containing known concentrations of method analytes derived from externally

prepared test materials. The QCS is obtained from a source external to the laboratory and is used to check laboratory performance.

4. INTERFERENCES

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

4.1.1 Isobaric elemental interferences - are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method (Table 4), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

4.1.2 Abundance sensitivity - is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.1.3 Isobaric polyatomic ion interferences - are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified[3], and these are listed in Table 2 together with the method

elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.1.4 Physical interferences - are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma - mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.2% (w/v) have been recommended[3] to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects[4]. Internal standards should have similar analytical behavior to the elements being determined.

4.1.5 Memory interferences - result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (see 7.6.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit, should be noted.
Memory interferences may also be assessed within an

analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be re-analyzed after a long rinse period.

5. SAFETY

5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method[5,6]. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis.

5.2 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards.

6. APPARATUS AND EQUIPMENT

6.1 INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETER

6.1.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

6.1.2 Argon gas supply (high-purity grade, 99.99%).

6.1.3 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.

6.1.4 A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g. from polyatomic oxide species).

6.1.5 Operating conditions - because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to

maintain quality control data verifying instrument performance and analytical results. Instrument operating conditions which were used to generate precision and accuracy data for this method (section 13) are included in Table 6.

6.1.6 Where necessary, precautions should be taken to protect the electron multiplier from exposure to high ion counts. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range and with isotopes falling within scanning windows should be diluted prior to analysis.

6.4 LABWARE - For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area, designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (i) contributing contaminants through surface desorption or leaching, (ii) depleting element concentrations through adsorption processes. All re-useable labware (glass, quartz, polyethylene, Teflon etc.) including the sample container should be cleaned prior to use. Labware should be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with water, ASTM type I water and oven drying.
NOTE: *chromic acid must not be used for the cleaning of glassware.*

6.4.1 Glassware - volumetric flasks and graduated cylinders.

6.4.2 Assorted calibrated pipettes.

6.4.3 Conical Phillips beakers, 250ml with 50 mm watch glasses. Griffin beakers, 250ml with 75 mm watch glasses.

6.4.4 Storage bottles - narrow mouth bottles, Teflon FEP (fluorinated ethylene propylene) with Tefzel ETFE (ethylene tetrafluorethylene) screw closure, 125ml and 250ml capacities.

6.4.5 Wash bottle - one piece stem, Teflon FEP bottle with Tefzel ETFE screw closure, 125ml capacity.

6.5 SAMPLE PROCESSING EQUIPMENT

6.5.1 Balance - analytical, capable of accurately weighing to 0.1mg.

6.5.2 Hot Plate - (Corning PC100 or equivalent).

6.5.3 Centrifuge - steel cabinet with guard bowl, electric timer and brake.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Reagents may contain elemental impurities which might affect analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used (Table 2), however, it should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

7.1.2 Nitric acid (1+1) - dilute 500ml conc. nitric acid to 1000ml with ASTM type I water.

7.1.3 Nitric acid (1+9) - dilute 100ml conc. nitric acid to 1000ml with ASTM type I water.

7.1.4 Hydrochloric acid, concentrated (sp.gr. 1.19).

7.1.5 Hydrochloric acid (1+4) - dilute 200ml conc. hydrochloric acid to 1000ml with ASTM type I water.

7.1.6 Ammonium hydroxide, concentrated (sp.gr. 0.902).

7.2 WATER - For all sample preparation and dilutions, ASTM type I water (ASTM D1193) is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 STANDARD STOCK SOLUTIONS - May be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99 - 99.999% pure). All salts should be dried for one hour at 105°C, unless otherwise specified. (CAUTION: Many metal salts are extremely toxic if inhaled or

swallowed. Wash hands thoroughly after handling). Stock solutions should be stored in Teflon bottles.

The following procedures may be used for preparing standard stock solutions:

NOTE: Some metals, particularly those which form surface oxides require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.3.1 Aluminum solution, stock 1ml = 1000 µg Al: Pickle aluminum metal in warm (1+1) HCl to an exact weight of 0.100g. Dissolve in 10ml conc. HCl and 2ml conc. nitric acid, heating to effect solution. Continue heating until volume is reduced to 4ml. Cool and add 4ml ASTM type I water. Heat until the volume is reduced to 2ml. Cool and dilute to 100ml with ASTM type I water.

7.3.2 Antimony solution, stock 1ml = 1000 µg Sb: Dissolve 0.100g antimony powder in 2ml (1+1) nitric acid and 0.5ml conc. hydrochloric acid, heating to effect solution. Cool, add 20ml ASTM type I water and 0.15g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100ml with ASTM type I water.

7.3.3 Arsenic solution, stock 1ml = 1000 µg As: Dissolve 0.1320g As_2O_3 in a mixture of 50ml ASTM type I water and 1ml conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify the solution with 2ml conc. nitric acid. Dilute to 100ml with ASTM type I water.

7.3.4 Barium solution, stock 1ml = 1000 µg Ba: Dissolve 0.1437g $BaCO_3$ in a solution mixture of 10ml ASTM type I water and 2ml conc. nitric acid. Heat and stir to effect solution and degassing. Dilute to 100ml with ASTM type I water.

7.3.5 Beryllium solution, stock 1ml = 1000 µg Be: Dissolve 1.965g $BeSO_4.4H_2O$ (DO NOT DRY) in 50ml ASTM Type I water. Add 1ml conc. nitric acid. Dilute to 100ml with ASTM type I water.

7.3.6 Bismuth solution, stock 1ml = 1000 µg Bi: Dissolve 0.1115g Bi_2O_3 in 5ml conc. nitric acid. Heat to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.7 Cadmium solution, stock 1ml = 1000 µg Cd: Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.8 Chromium solution, stock 1ml = 1000 µg Cr: Dissolve 0.1923g CrO_3 in a solution mixture of 10ml ASTM type I water and 1ml conc. nitric acid. Dilute to 100ml with ASTM type I water.

7.3.9 Cobalt solution, stock 1ml = 1000 µg Co: Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.10 Copper solution, stock 1ml = 1000 µg Cu: Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.11 Indium solution, stock 1ml = 1000 µg In: Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100g. Dissolve in 10ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.12 Lead solution, stock 1ml = 1000 µg Pb: Dissolve 0.1599g $PbNO_3$ in 5ml (1+1) nitric acid. Dilute to 100ml with ASTM type I water.

7.3.13 Magnesium solution, stock 1ml = 1000 µg Mg: Dissolve 0.1658g MgO in 10ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.14 Manganese solution, stock 1ml = 1000 µg Mn: Pickle manganese flake in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.15 Molybdenum solution, stock 1ml = 1000 µg Mo: Dissolve 0.1500g MoO_3 in a solution mixture of 10ml ASTM type I water and 1ml conc. ammonium hydroxide., heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.16 Nickel solution, stock 1ml = 1000 µg Ni: Dissolve 0.100g nickel powder in 5ml conc. nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.17 Scandium solution, stock 1ml = 1000 µg Sc: Dissolve 0.1534g Sc_2O_3 in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.18 Selenium solution, stock 1ml = 1000 µg Se: Dissolve 0.1405g SeO_2 in 20ml ASTM type I water. Dilute to 100ml with ASTM type I water.

7.3.19 Silver solution, stock 1ml = 1000 µg Ag: Dissolve 0.100g silver metal in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water. Store in amber container.

7.3.20 Terbium solution, stock 1ml = 1000 µg Tb: Dissolve 0.1176g Tb_4O_7 in 5ml conc. nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.21 Thallium solution, stock 1ml = 1000 µg Tl: Dissolve 0.1303g $TlNO_3$ in a solution mixture of 10ml ASTM type I water and 1ml conc. nitric acid. Dilute to 100ml with ASTM type I water.

7.3.22 Thorium solution, stock 1ml = 1000 µg Th: Dissolve 0.2380g $Th(NO_3)_4.4H_2O$ (DO NOT DRY) in 20ml ASTM type I water. Dilute to 100ml with ASTM type I water.

7.3.23 Uranium solution, stock 1ml = 1000 µg U: Dissolve 0.2110g $UO_2(NO_3)_2.6H_2O$ (DO NOT DRY) in 20ml ASTM type I water and dilute to 100ml with ASTM type I water.

7.3.24 Vanadium solution, stock 1ml = 1000 µg V: Pickle vanadium metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.25 Yttrium solution, stock 1ml = 1000 µg Y: Dissolve 0.1270g Y_2O_3 in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.3.26 Zinc solution, stock 1ml = 1000 µg Zn: Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100g. Dissolve in 5ml (1+1) nitric acid, heating to effect solution. Cool and dilute to 100ml with ASTM type I water.

7.4 MULTI-ELEMENT STOCK STANDARD SOLUTIONS - Care must be taken in the preparation of multi-element stock standards that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid cleaned, not previously used FEP fluoro-carbon bottles for storage and monitored periodically for stability. The following combinations of elements are suggested:

Standard Solution A		Standard Solution B
Aluminum	Manganese	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	

Multi-element stock standard solutions A and B (1ml = 10 µg) may be prepared by diluting 1ml of each single element stock in the combination list to 100ml with ASTM type I water containing 1% (v/v) nitric acid.

7.4.1 Preparation of calibration standards - fresh multi-element calibration standards should be prepared every two weeks or as needed. Dilute each of the stock multi-element standard solutions A and B to levels appropriate to the operating range of the instrument using ASTM type I water containing 1% (v/v) nitric acid. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. Concentrations of 200 µg/l are suggested. If the spiking procedure is being used (9.2.1), add internal standards (7.5) to the calibration standards and store in Teflon bottles. Calibration standards should be initially verified using a quality control sample (7.8).

7.5 INTERNAL STANDARDS STOCK SOLUTION, 1ml = 100 µg. Dilute 10ml of scandium, yttrium, indium, terbium and bismuth stock standards (7.3) to 100ml with ASTM type I water, and store in a Teflon bottle. Use this solution concentrate to spike blanks, calibration standards and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump (9.2.2).

7.6 BLANKS - Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

7.6.1 Calibration blank - consists of 1% (v/v) nitric acid in ASTM type I water. If the spiking procedure is being used (9.2.1) add internal standards.

7.6.2 Laboratory reagent blank (preparation blank) - must contain all the reagents in the same volumes as used in processing the samples. The preparation blank must be carried through the entire sample digestion and preparation scheme. If the spiking procedure (9.2.1) is being used, add internal standards to the solution after the preparation is complete.

7.6.3 Rinse blank - consists of 2% (v/v) nitric acid in ASTM type I water.

7.7 TUNING SOLUTION - This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions (see 7.3) in 1% (v/v) nitric acid to produce a concentration of 100 µg/l of each element. Internal standards are not added to this solution.

7.8 QUALITY CONTROL SAMPLE - The quality control sample will be available from the Quality Assurance Branch EMSL-Cincinnati. Dilute an appropriate aliquot of analytes (concentrations not to exceed 1000 µg/l), in 1% (v/v) nitric acid. If the spiking procedure (9.2.1) is being used, add internal standards after dilution, mix and store in a Teflon bottle.

7.9 LABORATORY FORTIFIED BLANK - To an aliquot of reagent blank, add aliquots from multi-element stock standards A and B (7.4) to produce a final concentration of 200 µg/l for each analyte. The fortified blank must be carried through the entire sample digestion and preparation scheme. If the spiking procedure (9.2.1) is being used, add internal standards to this solution after preparation has been completed.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Prior to the collection of the sample, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation etc. should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 For the determination of dissolved elements, the sample should be filtered through a 0.45 µm membrane filter. Use a portion of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to a pH of less than 2.

8.3 For the determination of total recoverable elements in aqueous samples, acidify with (1+1) nitric acid at the time of

collection to a pH of less than 2. The sample should not be filtered prior to analysis.

NOTE: Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions, should be acidified with nitric acid to a pH of less than 2 upon receipt in the laboratory (normally, 3ml of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). Following acidification, the sample should be held for sixteen hours before withdrawing an aliquot for sample processing.

8.4 Solid samples usually require no preservation prior to analysis other than storage at 4°C.

9. CALIBRATION AND STANDARDIZATION

9.1 CALIBRATION - Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed, and at requisite intervals.

9.1.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than thirty minutes for the instrument to warm up. During this process conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24,25,26. Resolution at high mass is indicated by lead isotopes 206,207,208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

9.1.2 Instrument stability must be demonstrated by running the tuning solution (7.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

9.1.2 Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated for the analytes to be determined using the calibration blank (7.6.1) and calibration standards A and B (7.4.1) prepared at one or more concentration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

9.1.3 The rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Allow sufficient rinse time to remove traces of the previous sample or a minimum of one minute. Solutions should be aspirated for thirty seconds prior to the acquisition of data to allow equilibrium to be established.

9.2 INTERNAL STANDARDIZATION - Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 3. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application, detail the use of five internal standards; scandium, yttrium, indium, terbium and bismuth. These were used to generate the precision and recovery data attached to this method. Internal standards must be present in all samples, standards and blanks at identical levels. This may be achieved by adding an aliquot spike of internal standards to the solution (method 9.2.1), or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil (method 9.2.2). The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. A concentration of 200 µg/l of each internal standard is recommended. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

9.3 INSTRUMENT PERFORMANCE - Check the performance of the instrument and verify the calibration using data gathered from analyses of calibration blanks, calibration standards and the quality control sample.

9.3.1 After the calibration has been established, it must be initially verified for all analytes by analyzing the QCS (7.8). If measurements exceed ± 10% of the established QCS value, the analysis should be terminated, the source of the problem identified and corrected, the instrument re-calibrated and the calibration re-verified before continuing analyses.

9.3.2 To verify that the instrument is properly calibrated on a continuing basis, run the calibration blank and calibration standards as surrogate samples after every ten analyses. The results of the analyses of the standards will indicate whether the calibration remains valid. If the indicated concentration of any analyte deviates from

the true concentration by more than 10%, the instrument must be recalibrated and the previous ten samples re-analyzed. The instrument responses from the calibration check may be used for recalibration purposes. If the sample matrix is responsible for the calibration drift, it is recommended that the previous ten samples are re-analyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

10.2 INITIAL DEMONSTRATION OF PERFORMANCE.

10.2.1 The initial demonstration of performance is used to characterize instrument performance (method detection limits and linear calibration ranges) for analyses conducted by this method.

10.2.2 Method detection limits (MDL) - method detection limits should be established for all analytes, using reagent water (blank) spiked at a concentration of two to five times the estimated detection limit[7]. To determine MDL values, take seven replicate aliquots of the spiked reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

Method detection limits should be determined every six months or whenever a significant change in background or instrument response is expected (e.g. detector change).

10.2.3 Linear calibration ranges - linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response is expected (e.g. detector change).

10.3 ASSESSING LABORATORY PERFORMANCE - REAGENT AND FORTIFIED BLANKS

10.3.1 Laboratory reagent blank (LRB) - the laboratory must analyze at least one reagent blank (7.6.2) with each set of samples. Reagent blank data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples re-analyzed.

10.3.2 Laboratory fortified blank (LFB) - the laboratory must analyze at least one fortified blank (7.9) with each batch of samples. Calculate accuracy as percent recovery (see 10.4.2) If the recovery of any analyte falls outside the control limits (see 10.3.3), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.3.3 Until sufficient data become available from within their own laboratory (usually a minimum of twenty to thirty analyses), the laboratory should assess laboratory performance against recovery limits of 85 - 115%. When sufficient internal performance data becomes available, develop control limits from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = x + 3S$$
$$\text{LOWER CONTROL LIMIT} = x - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent twenty to thirty data points.

10.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.4.1 The laboratory must add a known spike to a minimum of 10% of the routine samples or one sample spike per set, whichever is greater. Ideally for water samples, the analyte concentration should be the same as that used in the laboratory fortified blank (10.3.2). For solid samples, the concentration added should be 100 mg/kg equivalent (200 µg/l in the analysis solution). Over time, samples from all routine sample sources should be spiked.

10.4.2 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unspiked sample, and compare these values to the control limits established in section 10.3.3 for the analyses of LFBs. Spike recovery calculations are not required if the spike concentration is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery.
C_s = spiked sample concentration.
C = sample background concentration.
s = concentration equivalent of spike added to sample.

10.4.3 If the recovery of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (section 10.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unspiked sample must be labelled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.5 INTERNAL STANDARDS RESPONSES - The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should be monitored routinely in order to detect potential problems caused by mass dependent drift, errors incurred in solution spiking or increases in the concentrations of individual internal standards caused by background contributions from the sample.
The absolute response of any one internal standard should not

deviate more than 60-125% of the original response in the calibration blank. If deviations greater than this are observed, use the following test procedure:

10.5.1 Flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, re-spike with internal standards and re-analyze.

10.5.2 If test 10.5.1 is not satisfied, or if it is a blank or calibration standard that is out of limits, terminate the analysis, and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

11. PROCEDURE

11.1 SAMPLE PREPARATION - DISSOLVED ELEMENTS.

11.1.1 For the determination of dissolved elements in drinking water, ground and surface waters, take a 100ml aliquot of the filtered acid preserved sample, and add 1ml of concentrated nitric acid. If the spiking procedure (9.2.1) is being used, add internal standards and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations. NOTE: If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using the procedure in section 11.2.1 prior to analysis.

11.2 SAMPLE PREPARATION - TOTAL RECOVERABLE ELEMENTS.

11.2.1 For the determination of total recoverable elements in water or wastewater, take a 100ml aliquot from a well mixed, acid preserved, sample containing not more than 0.25% (w/v) total solids and transfer to a 250ml Griffin beaker. (If total solids are greater than 0.25% reduce the size of the aliquot by a proportionate amount). Add 1ml of conc. nitric acid and 0.5ml conc. hydrochloric acid. Heat on a hot plate until the volume has been reduced to 15-20ml, ensuring that the sample does not boil (NOTE: A spare beaker containing approximately 15ml of water can be used as a gauge. Evaporation time for 100ml of sample at 85°C is approximately one and a half hours). Cover the beaker with a watch glass and reflux for thirty minutes (very slight boiling may occur).

Allow to cool and transfer to a 50ml volumetric flask. Dilute to volume with ASTM type I water. Centrifuge the sample or allow to stand overnight to separate insoluble material. Prior to analysis, pipette 20ml into a 50ml volumetric flask and dilute to volume with ASTM type I water. If the spiking procedure (9.2.1) is being used, add internal standards and mix. The sample is now ready for analysis. Analysis should be performed within seventy two hours of the completed preparation.

11.2.2 For the determination of total recoverable elements in solid samples (sludge, soils, sediments), mix the sample thoroughly to achieve homogeneity and weigh accurately a 1.0 $\pm$ 0.01 g portion of the sample. Transfer to a 250 ml Phillips beaker. Add 4ml (1+1) nitric acid and 10ml (1+4) HCl. Cover with a watch glass. Heat the sample on a hot plate at 95°C and gently reflux for thirty minutes (very slight boiling may occur). Allow the sample to cool, transfer to a 100ml volumetric flask. Dilute to volume with ASTM type I water. Centrifuge the sample or allow to stand overnight to separate insoluble material. Prior to analysis, pipette 10ml into a 50ml volumetric flask and dilute to volume with ASTM type I water. If the spiking procedure (9.2.1) is being used, add internal standards and mix. The sample is now ready for analysis. Analysis should be performed within seventy two hours of the completed preparation.
NOTE: Determine the percent solids in the sample for use in calculations and for reporting data on a dry weight basis.

11.3 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen for high element concentrations. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the linear range. Matrix screening may be carried out by using intelligent software, if available, or by diluting the sample by a factor of 500 and analyzing in a semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of the analytical data.

11.4 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest (see section 9).

11.5 Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Discard any integrations which are considered to be statistical outliers and use the average of the integrations for data reporting.

11.6 All masses which might affect data quality must be monitored during the analytical run. As a minimum, those masses prescribed in Table 4 must be monitored in the same scan as is used for the collection of the data. This information should be used to correct the data for identified interferences.

11.7 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute. Samples should be aspirated for thirty seconds prior to the collection of data.

11.8 Samples having concentrations higher than the established linear dynamic range should be diluted into range and re-analyzed. The sample should first be analyzed for the trace elements in the sample, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided quality control data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

12. CALCULATIONS

12.1 Elemental equations recommended for sample data calculations are listed in Table 5. Sample data should be reported in units of µg/l for aqueous samples or mg/kg dry weight for solid samples. Do not report element concentrations below the determined MDL.

12.2 For data values less than ten, two significant figures should be used for reporting element concentrations. For data values greater than or equal to ten, three significant figures should be used.

12.3 Reported values should be calibration blank subtracted. For aqueous samples prepared by total recoverable procedure 11.2.1, multiply solution concentrations by the dilution factor 1.25. For solid samples prepared by total recoverable procedure 11.2.2, multiply solution concentrations (µg/l in the analysis solution) by the dilution factor 0.5. If additional dilutions were made to any samples, the appropriate factor should be applied to the calculated sample concentrations.

12.4 Data values should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples,

regardless of the addition of hydrochloric acid, as the chloride ion is a common constituent of environmental samples.

12.5 If an element has more than one monitored isotope, examination of the concentrations calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, the secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

12.6 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13. PRECISION AND ACCURACY

13.1 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 6. Total recoverable method detection limits determined using the procedure described in 10.2.2, are listed in Table 7.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 8 for five water samples representing drinking water, surface water, ground water and waste effluent. Samples were prepared using the procedure described in 11.2.1. For each matrix, five replicates were analyzed and the average of the replicates used for determining the sample background concentration for each element. Two further pairs of duplicates were spiked at different concentration levels. For each method element, the sample background concentration, mean spike percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate spike determinations are listed in Table 8.

13.3 Data obtained from single laboratory testing of the method are summarized in Table 9 for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil and EPA Electroplating Sludge. Samples were prepared using the procedure described in 11.2.2. For each method element, the sample background concentration, mean spike percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate spikes were determined as for 13.2.

14. REFERENCES

1. A.L. Gray and A.R.Date, Analyst 108 1033 (1983).

2. R.S. Houk et al. Anal. Chem. 52 2283 (1980).

3. R.S. Houk, Anal. Chem. 58 97A (1986).

4. J.J. Thompson and R.S. Houk, Appl. Spec. 41 801 (1987).

5. "OSHA Safety and Health Standards, General Industry," (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

6. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986.

7. Code of Federal Regulations 40, Ch. 1, Pt. 136 Appendix B.

TABLE 1: ESTIMATED INSTRUMENT DETECTION LIMITS

METHOD 200.8

ELEMENT	RECOMMENDED ANALYTICAL MASS	ESTIMATED IDL (µg/l)
Aluminum	27	0.05
Antimony	121	0.08
Arsenic	75	0.9
Barium	137	0.5
Beryllium	9	0.1
Cadmium	111	0.1
Chromium	52	0.07
Cobalt	59	0.03
Copper	63	0.03
Lead	206,207,208	0.08
Manganese	55	0.1
Molybdenum	98	0.1
Nickel	60	0.2
Selenium	82	5
Silver	107	0.05
Thallium	205	0.09
Thorium	232	0.03
Uranium	238	0.02
Vanadium	51	0.02
Zinc	66	0.2

Instrument detection limits (3σ) estimated from seven replicate scans of the blank (1% v/v nitric acid) and three replicate scans of a multi-element standard using an integration time of one minute.

TABLE 2: COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

BACKGROUND MOLECULAR IONS.

Molecular Ion	Mass	Element Interference[9]
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	
CN^+	26	
CO^+	28	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se

[9] Method elements or internal standards affected by the molecular ions.

TABLE 2 (Continued).

MATRIX MOLECULAR IONS		
CHLORIDE		
Molecular Ion	**Mass**	**Element Interference**
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
SULPHATE		
Molecular Ion	**Mass**	**Element Interference**
$^{32}SO^+$	48	
$^{32}SOH^+$	49	
$^{34}SO^+$	50	V,Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	
PHOSPHATE		
Molecular Ion	**Mass**	**Element Interference**
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^+	71	
GROUP I, II METALS		
Molecular Ion	**Mass**	**Element Interference**
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	
MATRIX OXIDES*		
Molecular Ion	**Masses**	**Element Interference**
TiO	62-66	Ni,Cu,Zn
ZrO	106-112	Ag,Cd
MoO	108-116	Cd

* Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes are monitored in solid waste samples, likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 3: INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

Internal standards recommended for use with this method are shown in bold face. Preparation procedures for these are included in section 7.3.

TABLE 4 : RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES WHICH MUST BE MONITORED

Isotope	Element of Interest
27	Aluminum
121,123	Antimony
75	Arsenic
135,137	Barium
9	Beryllium
106,108,111,114	Cadmium
52,53	Chromium
59	Cobalt
63,65	Copper
206,207,208	Lead
55	Manganese
95,97,98	Molybdenum
60,62	Nickel
77,82	Selenium
107,109	Silver
203,205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66,67,68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

NOTE: Isotopes recommended for analytical determination are underlined.

TABLE 5 (Continued).

INTERNAL STANDARDS

Element	Elemental Equation	Note
Bi	$(1.000)(^{209}C)$	
In	$(1.000)(^{115}C)-(0.016)(^{118}C)$	(8)
Sc	$(1.000)(^{45}C)$	
Tb	$(1.000)(^{159}C)$	
Y	$(1.000)(^{89}C)$	

C - calibration blank subtracted counts at specified mass.
(1) - correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
(2) - correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.
(3) - in 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
(4) - allowance for isotopic variability of lead isotopes.
(5) - isobaric elemental correction for ruthenium.
(6) - some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
(7) - correction for chloride interference with adjustment for Cr53. ClO 51/53 ratio may be determined from the reagent blank.
(8) - isobaric elemental correction for tin.

TABLE 5 : RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{121}C)$	
As	$(1.000)(^{75}C)-(3.127)[(^{77}C)-(0.815)(^{82}C)]$	(1)
Ba	$(1.000)(^{137}C)$	
Be	$(1.000)(^{9}C)$	
Cd	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(2)
Cr	$(1.000)(^{52}C)$	(3)
Co	$(1.000)(^{59}C)$	
Cu	$(1.000)(^{63}C)$	
Pb	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(4)
Mn	$(1.000)(^{55}C)$	
Mo	$(1.000)(^{98}C)-(0.146)(^{99}C)$	(5)
Ni	$(1.000)(^{60}C)$	
Se	$(1.000)(^{82}C)$	(6)
Ag	$(1.000)(^{107}C)$	
Tl	$(1.000)(^{205}C)$	
Th	$(1.000)(^{232}C)$	
U	$(1.000)(^{238}C)$	
V	$(1.000)(^{51}C)-(3.127)((^{53}C)-(0.113)(^{52}C))$	(7)
Zn	$(1.000)(^{66}C)$	

Cont.

TABLE 5 : RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{121}C)$	
As	$(1.000)(^{75}C)-(3.127)[(^{77}C)-(0.815)(^{82}C)]$	(1)
Ba	$(1.000)(^{137}C)$	
Be	$(1.000)(^{9}C)$	
Cd	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(2)
Cr	$(1.000)(^{52}C)$	(3)
Co	$(1.000)(^{59}C)$	
Cu	$(1.000)(^{63}C)$	
Pb	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(4)
Mn	$(1.000)(^{55}C)$	
Mo	$(1.000)(^{98}C)-(0.146)(^{99}C)$	(5)
Ni	$(1.000)(^{60}C)$	
Se	$(1.000)(^{82}C)$	(6)
Ag	$(1.000)(^{107}C)$	
Tl	$(1.000)(^{205}C)$	
Th	$(1.000)(^{232}C)$	
U	$(1.000)(^{238}C)$	
V	$(1.000)(^{51}C)-(3.127)((^{53}C)-(0.113)(^{52}C))$	(7)
Zn	$(1.000)(^{66}C)$	

Cont.

TABLE 7: TOTAL RECOVERABLE METHOD DETECTION LIMITS

ELEMENT	RECOMMENDED ANALYTICAL MASS	MDL+ AQUEOUS µg/l	MDL+ SOLIDS mg/kg
Aluminum	27	1.0	0.4
Antimony	121	0.4	0.2
Arsenic	75	1.4	0.6
Barium	137	0.8	0.4
Beryllium	9	0.3	0.1
Cadmium	111	0.5	0.2
Chromium	52	0.9	0.4
Cobalt	59	0.09	0.04
Copper	63	0.5	0.2
Lead	206,207,208	0.6	0.3
Manganese	55	0.1	0.05
Molybdenum	98	0.3	0.1
Nickel	60	0.5	0.2
Selenium	82	7.9	3.2
Silver	107	0.1	0.05
Thallium	205	0.3	0.1
Thorium	232	0.1	0.05
Uranium	238	0.1	0.05
Vanadium	51	2.5	1.0
Zinc	66	1.8	0.7

+ MDL concentrations are computed for original matrix with allowance for sample dilution during preparation.

TABLE 6: INSTRUMENT OPERATING CONDITIONS FOR PRECISION AND ACCURACY DATA

Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 l/min.
Auxiliary flow rate	0.6 l/min.
Nebulizer flow rate	0.78 l/min.
Solution uptake rate	0.6 ml/min.
Spray chamber temperature	15 °C
Data Acquisition	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 - 240 amu
Dwell time	320 µs
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 minutes per sample

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

WELL WATER

Element	Sample Concn. (µg/l)	Low Spike (µg/l)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/l)	Average Recovery R (%)	S(R)	RPD
Al	34.3	50	100.1	3.9	0.8	200	102.6	1.1	1.3
Sb	0.46	10	98.4	0.9	1.9	100	102.5	0.7	1.9
As	<1.4	50	110.0	6.4	16.4	200	101.3	0.2	0.5
Ba	106	50	95.4	3.9	3.3	200	104.9	1.0	1.6
Be	<0.3	10	104.5	0.4	1.0	100	101.4	1.2	3.3
Cd	1.6	10	88.6	1.7	3.8	100	98.6	0.6	1.6
Cr	<0.9	10	111.0	0.0	0.0	100	103.5	0.4	1.0
Co	2.4	10	100.6	1.0	1.6	100	104.1	0.4	0.9
Cu	37.4	10	104.3	5.1	1.5	100	100.6	0.8	1.5
Pb	3.5	10	95.2	2.5	1.5	100	99.5	1.4	3.9
Mn	2770	10	*	*	1.8	100	*	*	0.7
Mo	2.1	10	103.8	1.1	1.6	100	102.9	0.7	1.9
Ni	11.4	10	116.5	6.3	6.5	100	99.6	0.3	0.0
Se	<7.9	50	127.3	8.4	18.7	200	101.3	0.2	0.5
Ag	<0.1	50	99.2	0.4	1.0	200	101.5	1.4	3.9
Tl	<0.3	10	93.9	0.1	0.0	100	100.4	1.8	5.0
Th	<0.1	10	103.0	0.7	1.9	100	104.5	1.8	4.8
U	1.8	10	106.0	1.1	1.6	100	109.7	2.5	6.3
V	<2.5	50	105.3	0.8	2.1	200	105.8	0.2	0.5
Zn	554	50	*	*	1.2	200	102.1	5.5	3.2

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

DRINKING WATER

Element	Sample Concn. (µg/l)	Low Spike (µg/l)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/l)	Average Recovery R (%)	S(R)	RPD
Al	175	50	115.8	5.9	0.4	200	102.7	1.6	1.1
Sb	<0.4	10	99.1	0.7	2.0	100	100.8	0.7	2.0
As	<1.4	50	99.7	0.8	2.2	200	102.5	1.1	2.9
Ba	43.8	50	94.8	3.9	5.8	200	95.6	0.8	1.7
Be	<0.3	10	113.5	0.4	0.9	100	111.0	0.7	1.8
Cd	<0.5	10	97.0	2.8	8.3	100	101.5	0.4	1.0
Cr	<0.9	10	111.0	3.5	9.0	100	99.5	0.1	0.2
Co	0.11	10	94.4	0.4	1.1	100	93.6	0.5	1.4
Cu	3.6	10	101.8	8.8	17.4	100	91.6	0.3	0.3
Pb	0.87	10	97.8	2.0	2.8	100	99.0	0.8	2.2
Mn	0.96	10	96.9	1.8	4.7	100	95.8	0.6	1.8
Mo	1.9	10	99.4	1.6	3.4	100	98.6	0.4	1.0
Ni	1.9	10	100.2	5.7	13.5	100	95.2	0.5	1.3
Se	<7.9	50	99.0	1.8	5.3	200	93.5	3.5	10.7
Ag	<0.1	50	100.7	1.5	4.2	200	99.0	0.4	1.0
Tl	<0.3	10	97.5	0.4	1.0	100	98.5	1.7	4.9
Th	<0.1	10	109.0	0.7	1.8	100	106.0	1.4	3.8
U	0.23	10	110.7	1.4	3.5	100	107.8	0.7	1.9
V	<2.5	50	101.4	0.1	0.4	200	97.5	0.7	2.1
Zn	5.2	50	103.4	3.3	7.7	200	96.4	0.5	1.0

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND ACCURACY DATA IN AQUEOUS MATRICES (Cont).

SEWAGE TREATMENT PRIMARY EFFLUENT

Element	Sample Concn. (µg/l)	Low Spike (µg/l)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/l)	Average Recovery R (%)	S(R)	RPD
Al	1150	50	*	*	3.5	200	100.0	13.8	1.5
Sb	1.5	10	95.7	0.4	0.9	100	104.5	0.7	1.9
As	<1.4	50	104.2	4.5	12.3	200	101.5	0.7	2.0
Ba	202	50	79.2	9.9	2.5	200	108.6	4.6	5.5
Be	<0.3	10	110.5	1.8	4.5	100	106.4	0.4	0.9
Cd	9.2	10	101.2	1.3	0.0	100	102.3	0.4	0.9
Cr	128	10	*	*	1.5	100	102.1	1.7	0.4
Co	13.4	10	95.1	2.7	2.2	100	99.1	1.1	2.7
Cu	171	10	*	*	2.4	100	105.2	7.1	0.7
Pb	17.8	10	95.7	3.8	1.1	100	102.7	1.1	2.5
Mn	199	10	*	*	1.5	100	103.4	2.1	0.7
Mo	136	10	*	*	1.4	100	105.7	2.4	2.1
Ni	84.0	10	88.4	16.3	4.1	100	98.0	0.9	0.0
Se	<7.9	50	112.0	10.9	27.5	200	108.8	3.0	7.8
Ag	10.9	50	97.1	0.7	1.5	200	102.6	1.4	3.7
Tl	<0.3	10	97.5	0.4	1.0	100	102.0	0.0	0.0
Th	0.11	10	15.4	1.8	30.3	100	29.3	0.8	8.2
U	0.71	10	109.4	1.8	4.3	100	109.3	0.7	1.8
V	<2.5	50	90.9	0.9	0.6	200	99.4	2.1	6.0
Zn	163	50	85.8	3.3	0.5	200	102.0	1.5	1.9

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND ACCURACY DATA IN AQUEOUS MATRICES (Cont).

POND WATER

Element	Sample Concn. (µg/l)	Low Spike (µg/l)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/l)	Average Recovery R (%)	S(R)	RPD
Al	610	50	*	*	1.7	200	78.2	9.2	5.5
Sb	<0.4	10	101.1	1.1	2.9	100	101.5	3.0	8.4
As	<1.4	50	100.8	2.0	5.6	200	96.8	0.9	2.6
Ba	28.7	50	102.1	1.8	2.4	200	102.9	3.7	9.0
Be	<0.3	10	109.1	0.4	0.9	100	114.4	3.9	9.6
Cd	<0.5	10	106.6	3.2	8.3	100	105.8	2.8	7.6
Cr	2.0	10	107.0	1.0	1.6	100	100.0	1.4	3.9
Co	0.79	10	101.6	1.1	2.7	100	101.7	1.8	4.9
Cu	5.4	10	107.5	1.4	1.9	100	98.1	2.5	6.8
Pb	1.9	10	108.4	1.5	3.2	100	106.1	0.0	0.0
Mn	617	10	*	*	1.1	100	139.0	11.1	4.0
Mo	0.98	10	104.2	1.4	3.5	100	104.0	2.1	5.7
Ni	2.5	10	102.0	2.3	4.7	100	102.5	2.1	5.7
Se	<7.9	50	102.7	5.6	15.4	200	105.5	1.4	3.8
Ag	0.12	50	102.5	0.8	2.1	200	105.2	2.7	7.1
Tl	<0.3	10	108.5	3.2	8.3	100	105.0	2.8	7.6
Th	0.19	10	93.1	3.5	10.5	100	93.9	1.6	4.8
U	0.30	10	107.0	2.8	7.3	100	107.2	1.8	4.7
V	3.5	50	96.1	5.2	14.2	200	101.5	0.2	0.5
Zn	6.8	50	99.8	1.7	3.7	200	100.1	2.8	7.7

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 8 : PRECISION AND ACCURACY DATA IN AQUEOUS MATRICES (Cont).

INDUSTRIAL EFFLUENT

Element	Sample Concn. (µg/l)	Low Spike (µg/l)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/l)	Average Recovery R (%)	S(R)	RPD
Al	44.7	50	98.8	8.7	5.7	200	90.4	2.1	2.2
Sb	2990	10	*	*	0.3	100	*	*	0.0
As	<1.4	50	75.1	1.8	6.7	200	75.0	0.0	0.0
Ba	100	50	96.7	5.5	3.4	200	102.9	1.1	0.7
Be	<0.3	10	103.5	1.8	4.8	100	100.0	0.0	0.0
Cd	10.1	10	106.5	4.4	2.4	100	97.4	1.1	2.8
Cr	171	10	*	*	0.0	100	127.7	2.4	1.7
Co	1.3	10	90.5	3.2	8.7	100	90.5	0.4	1.3
Cu	101	10	*	*	0.9	100	92.5	2.0	1.6
Pb	294	10	*	*	2.6	100	108.4	2.1	0.0
Mn	154	10	*	*	2.8	100	103.6	3.7	1.6
Mo	1370	10	*	*	1.4	100	*	*	0.7
Ni	17.3	10	107.4	7.4	5.0	100	88.2	0.7	1.0
Se	15.0	50	129.5	9.3	15.1	200	118.3	1.9	3.6
Ag	<0.1	50	91.8	0.6	1.7	200	87.0	4.9	16.1
Tl	<0.3	10	90.5	1.8	5.5	100	98.3	1.0	2.8
Th	0.29	10	109.6	1.2	2.7	100	108.7	0.0	0.0
U	0.17	10	104.8	2.5	6.6	100	109.3	0.4	0.9
V	<2.5	50	74.9	0.1	0.3	200	72.0	0.0	0.0
Zn	43.4	50	85.0	4.0	0.6	200	97.6	1.0	0.4

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 9 : PRECISION AND ACCURACY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5170	20	*	*	-	100	*	*	-
Sb	5.4	20	69.8	2.5	4.7	100	70.4	1.8	6.5
As	8.8	20	104.7	5.4	9.1	100	102.2	2.2	5.4
Ba	113	20	54.9	63.6	18.6	100	91.0	9.8	0.5
Be	0.6	20	100.1	0.6	1.5	100	102.9	0.4	1.0
Cd	1.8	20	97.3	1.0	1.4	100	101.7	0.4	1.0
Cr	83.5	20	86.7	16.1	8.3	100	105.5	1.3	0.0
Co	7.1	20	98.8	1.2	1.9	100	102.9	0.7	1.8
Cu	115	20	86.3	13.8	3.4	100	102.5	4.2	4.6
Pb	152	20	85.0	45.0	13.9	100	151.7	25.7	23.7
Mn	370	20	*	*	12.7	100	85.2	10.4	2.2
Mo	4.8	20	95.4	1.5	2.9	100	95.2	0.7	2.0
Ni	19.2	20	101.7	3.8	1.0	100	102.3	0.8	0.8
Se	<3.2	20	79.5	7.4	26.4	100	100.7	9.4	26.5
Ag	1.1	20	96.1	0.6	0.5	100	94.8	0.8	2.3
Tl	0.24	20	94.3	1.1	3.1	100	97.9	1.0	2.9
Th	1.0	20	69.8	0.6	1.3	100	76.0	2.2	7.9
U	1.1	20	100.1	0.2	0.0	100	102.9	0.0	0.0
V	17.8	20	109.2	4.2	2.3	100	106.7	1.3	2.4
Zn	128	20	87.0	27.7	5.5	100	113.4	12.9	14.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 9 : PRECISION AND ACCURACY DATA IN SOLID MATRICES (Cont).

NBS 1645 RIVER SEDIMENT

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5060	20	*	*	-	100	*	*	-
Sb	21.8	20	73.9	6.5	9.3	100	81.2	1.5	3.9
As	67.2	20	104.3	13.0	7.6	100	107.3	2.1	2.9
Ba	54.4	20	105.6	4.9	2.8	100	98.6	2.2	3.9
Be	0.59	20	88.8	0.2	0.5	100	87.9	0.1	0.2
Cd	8.3	20	92.9	0.4	0.0	100	95.7	1.4	3.9
Cr	29100	20	*	*	-	100	*	*	-
Co	7.9	20	97.6	1.3	2.6	100	103.1	0.0	0.0
Cu	112	20	121.0	9.1	1.5	100	105.2	2.2	1.8
Pb	742	20	*	*	-	100	-	-	-
Mn	717	20	*	*	-	100	-	-	-
Mo	17.1	20	89.8	8.1	12.0	100	98.4	0.7	0.9
Ni	41.8	20	103.7	6.5	4.8	100	102.2	0.8	0.0
Se	<3.2	20	108.3	14.3	37.4	100	93.9	5.0	15.1
Ag	1.8	20	94.8	1.6	4.3	100	96.2	0.7	1.9
Tl	1.2	20	91.2	1.3	3.6	100	94.4	0.4	1.3
Th	0.90	20	91.3	0.9	2.6	100	92.3	0.9	2.8
U	0.79	20	95.6	1.8	5.0	100	98.5	1.2	3.5
V	21.8	20	91.8	4.6	5.7	100	100.7	0.6	0.8
Zn	1780	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 9 : PRECISION AND ACCURACY DATA IN SOLID MATRICES (Cont).

EPA ELECTROPLATING SLUDGE #286

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5110	20	*	*	-	100	*	*	-
Sb	8.4	20	55.4	1.5	4.1	100	61.0	0.2	0.9
As	41.8	20	91.0	2.3	1.7	100	94.2	0.8	1.5
Ba	27.3	20	1.8	7.1	8.3	100	0	1.5	10.0
Be	0.25	20	92.0	0.9	2.7	100	93.4	0.3	0.9
Cd	112	20	85.0	5.2	1.6	100	88.5	0.8	0.5
Cr	7980	20	*	*	-	100	*	*	-
Co	4.1	20	89.2	1.8	4.6	100	88.7	1.5	4.6
Cu	740	20	*	*	6.0	100	61.7	20.4	5.4
Pb	1480	20	*	*	-	100	*	*	-
Mn	295	20	*	*	-	100	-	-	-
Mo	13.3	20	82.9	1.2	1.3	100	89.2	0.4	1.0
Ni	450	20	*	*	6.8	100	83.0	10.0	4.5
Se	3.5	20	89.7	3.7	4.2	100	91.0	6.0	18.0
Ag	5.9	20	89.8	2.1	4.6	100	85.1	0.4	1.1
Tl	1.9	20	96.9	0.9	2.4	100	98.9	0.9	2.4
Th	3.6	20	91.5	1.3	3.2	100	97.4	0.7	2.0
U	2.4	20	107.7	2.0	4.6	100	109.6	0.7	1.8
V	21.1	20	105.6	1.8	2.1	100	97.4	1.1	2.5
Zn	13300	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

METHOD 300.0
THE DETERMINATION OF INORGANIC ANIONS IN WATER BY ION CHROMATOGRAPHY

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INDEX

Section Number	Subject
1	Scope and Application
2	Summary of Method
3	Definitions
4	Interferences
5	Safety
6	Apparatus and Materials
7	Reagents and Consumable Materials
8	Sample Collection, Preservation and Storage
9	Calibration and Standardization
10	Quality Control
11	Procedure
12	Calculations
13	Precision and Accuracy
14	References

TABLES

1A. Chromatographic Conditions and Method Detection Limits in Reagent Water- for Part A
1B. Chromatographic Conditions and Method Detection Limits in Reagent Water- for Part B
2A. Single Operator Accuracy and Precision of Standard Anions
2B. Single Operator Accuracy and Precision of Chlorine Dioxide By-Products

FIGURES

1. Chromatogram Showing Separation Using the AS4A Column
2. Chromatogram Showing Separation Using the AS9 Column

METHOD 300.0
THE DETERMINATION OF INORGANIC ANIONS IN WATER BY ION CHROMATOGRAPHY

1. Scope and Application

1.1 This method covers the determination of the following inorganic anions.

PART A.	STORET NO. (Total)
Bromide	71870
Chloride	00940
Nitrate-N	00620
Nitrite-N	00615
Ortho-Phosphate-P	70507
Sulfate	00945

PART B.	STORET NO. (Total)
Chlorite	50074
Chlorate	-
Bromate	-

1.2 The matrices applicable to each method are shown below:

A. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 2.3), leachates (when no acetic acid is used 2.4)

B. Drinking water and reagent waters

1.3 The Method Detection Limit (MDL, defined in Section 13) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 10.2.

1.5 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.6.

2. Summary of Method

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

2.2 The main differences between Parts A and B are the separator columns, guard columns and eluents. Sections 6 and 7 will elicit the differences.

2.3 An extraction procedure must be performed to use this method for solids (See 11.7).

3. Definitions

3.1 Stock standard solution -- a concentrated solution containing a single certified standard that is a method analyte. Stock standard solutions are used to prepare calibration standards.

3.2 Calibration standards (CAL) -- a solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed, and used to calibrate the instrument response with respect to analytic concentration.

3.3 Quality control sample (QCS) -- a solution containing known concentrations of analytes, prepared by a laboratory other than the laboratory performing the analysis. The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

3.4 Performance evaluation sample (PE) -- a solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.5 Laboratory performance check standards (LPC) -- a solution of analytes prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 Laboratory duplicates (LD) -- two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

3.7 Field duplicates (FD) -- two samples taken at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.8 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

4. Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems.

4.2 The water dip or negative peak that elutes near and can interfere with the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5 This method is not recommended for fluoride. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5. Safety

5.1 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

6. Apparatus and Materials

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2 Anion separator column: This column produces the separation shown in Figures 1 and 2.

6.2.2.1 Anion separator column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of section 10.2 can be met.

6.2.2.2 Anion separator column (Method B). The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of section 10.2 can be met.

6.2.3 Anion suppressor device: The data presented in this method were generated using a Dionex anion micro membrane suppressor (P/N 37106).

6.2.4 Detector - Conductivity cell: approximately 1.25 µL internal volume, (Dionex, or equivalent) capable of providing data as required in section 10.2.

6.3 The Dionex AI-450 Data Chromatography Software (Version 2.0) was used to generate all the data in the attached tables. Systems using a stripchart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Section 10.2.

7. Reagents and Consumable Materials

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solutions:

7.3.1 Eluent solution (Method A): Sodium bicarbonate (CAS RN 144-55-8) 1.7 mM, sodium carbonate (CAS RN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 2 liters.

7.3.2 Eluent solution (Method B): Sodium bicarbonate (CAS RN 144-55-8) 0.2 mM, sodium carbonate (CAS RN 497-19-8) 1.4 mM. Dissolve 0.0336 g sodium bicarbonate ($NaHCO_3$) and 0.2968 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 2 liters.

7.4 Regeneration solution (micro membrane suppressor): Sulfuric acid (CAS RN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 liters with reagent water.

7.5 Stock standard solutions, 1000 mg/L (1 mg/ml): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as listed below.

7.5.1 Bromide (Br^-) 1000 mg/L: Dissolve 1.2876 g sodium bromide (NaBr, CAS RN 7647-15-6) in reagent water and dilute to 1 liter.

7.5.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 1.3057g of potassium bromate ($KBrO_3$, CAS RN 7758-01-2) in reagent water and dilute to 1 liter.

7.5.3 Chlorate (ClO_3^-) 1000 mg/L: Dissolve 1.2753g of sodium chlorate ($NaClO_3$, CAS RN 7775-09-9) in reagent water and dilute to 1 liter.

7.5.4 Chloride (Cl^-) 1000 mg/L: Dissolve 1.6485 g sodium chloride (NaCl, CAS RN 7647-14-5) in reagent water and dilute to 1 liter.

7.5.5 Chlorite (ClO_2^-) 1000 mg/L: Dissolve 1.3410g of sodium chlorite ($NaClO_2$, CAS RN 7758-19-2) in reagent water and dilute to 1 liter.

7.5.6 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$, CAS RN 7631-99-4) in reagent water and dilute to 1 liter.

7.5.7 Nitrite (NO_2^--N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$, CAS RN 7632-00-0) in reagent water and dilute to 1 liter.

7.5.8 Phosphate ($PO_4^{\equiv}$-P) 1000 mg/L: Dissolve 4.3937 g potassium phosphate (KH_2PO_4, CAS RN 7778-77-0) in reagent water and dilute to 1 liter.

7.5.9 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4, CAS RN 7778-80-5) in reagent water and dilute to 1 liter.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

8. Sample Collection, Preservation and Storage

8.1 Samples should be collected in scrupulously clean glass or polyethylene bottles.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follow:

Analyte	Preservation	Holding Time
Bromate	None required	28 days
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	immediately
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
O-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples be cooled to 4°C and held for no longer than 48 hours for Method A and analyze immediately in Method B.

9. Calibration and Standardization

9.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B.

9.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

9.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

9.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are

still more than ±10%, a new calibration curve must be prepared for that analyte.

9.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

10. Quality Control

10.1 Each laboratory using this method should have a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (10.2) and the analysis of fortified samples as a continuing check on performance. The laboratory should maintain performance records to define and document the quality of data that are generated.

10.1.1 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.1.2 The laboratory should fortify and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. A minimum of 10% of all samples should be run in duplicate.

10.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision data with this method, using a laboratory performance standard.

10.2.1 Select a representative check concentration for each analyte to be measured. Using stock standards, prepare a laboratory performance check sample concentrate in reagent water 100 times more concentrated than the selected concentrations.

10.2.2 Using a pipet, add 1.00 mL of the check sample concentrate (10.2.1) to each of a minimum of four 100-mL aliquots of reagent water. Analyze the aliquots according to the procedure in Section 11.

10.2.3 Calculate the average percent recovery (R), and the standard deviation(s) of the percent recovery, for the results.

10.2.4 Using the reagent water data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values calculated in Section 10.2.3. If the data are not comparable within

control limits (10.3.1), review potential problem areas and repeat the test.

10.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each laboratory fortified matrix of analyte being measured.

10.3.1 Calculate upper and lower control limits for method performance as follows:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

where R and s are calculated as in Section 10.2.3. The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

10.4 The laboratory should develop and maintain separate accuracy statements of laboratory performance for each matrix being analyzed by the laboratory. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analyses of four aliquots of each matrix, as described in Section 10.2.2, followed by the calculation of R and s.

10.5 Before processing any samples, the analyst must demonstrate through the analysis of an aliquot of reagent water that all glassware and reagent interferences are under control. Each time there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

10.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

10.7 In order to verify that standards have been prepared correctly a reference standard check should be performed using a standard of known concentration prepared by an independent source.

10.8 With each batch of samples processed analyze a single laboratory fortified blank containing each analyte of concern at a concentration at or near those used in the reagent water data in Tables 2A or 2B. If more than 20 samples are run in a batch

analyze one LFB for every 20 samples. Evaluate the accuracy by comparing to Tables 2A or 2B. If acceptable data cannot be obtained, locate the problem and correct it.

10.9 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

10.10 When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

11. Procedure

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 9.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for ten minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 μ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the users matrix through the use of fortified samples.

12. Calculation

12.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

12.2 Report results in mg/L.

12.3 Report NO_2^- as N
NO_3^- as N
$HPO_4^=$ as P

13. Precision and Accuracy - Method Detection Limit

13.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1A and 1B were obtained using reagent waters.

13.2 Single operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 2A and 2B.

14. References

14.1 "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. In Press.

14.2 Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography" proposed for the supplement 17th Edition of Standard Methods.

14.3 Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1988.

14.4 Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

Table 1A. Chromatographic Conditions and Detection Limits in Reagent Water (Part A)

Analyte	Peak #	* Retention Time(min)	MDL mg/L
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.1	0.002
o-Phosphate-P	6	5.3	0.003
Sulfate	7	6.8	0.02

Standard Conditions:

Columns: as specified in 6.2.2.1
Detector: as specified in 6.2.4
Eluent: as specified in 7.3.1

Pump Rate: 2.0 mL/min.
Sample Loop: 50μL

* MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1

Table 1B. Chromatographic Conditions and Detection Limits in Reagent Water(Part B)

Analyte	Peak # *	Retention Time(min)	MDL mg/L
Chlorite	1	2.8	0.01
Bromate	2	3.2	0.02
Chlorate	3	7.1	0.003

Standard Conditions:

Column: as specified in 6.2.2.2
Detector: as specified in 6.2.4
Eluent: as specified in 7.3.2

Pump Rate: 1.0 mL/min.
Sample Loop: 50uL

Attentuation - 1
y-axis - 500 ns

* See fig.2

Table 2A. Single-Operator Accuracy and Precision of Standard Anions (Part A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	99	0.08
	DW	5.0	7	105	0.10
	SW	5.0	7	95	0.13
	WW	5.0	7	105	0.34
	GW	5.0	7	92	0.34
	SD	2.0	7	82	0.06
Chloride	RW	20.0	7	96	0.35
	DW	20.0	7	108	1.19
	SW	10.0	7	86	0.33
	WW	20.0	7	101	5.2
	GW	20.0	7	114	1.3
	SD	20.0	7	90	0.32
Nitrate- N	RW	10.0	7	103	0.21
	DW	10.0	7	104	0.27
	SW	10.0	7	93	0.17
	WW	10.0	7	101	0.82
	GW	10.0	7	97	0.47
	SD	10.0	7	82	0.28
Nitrite- N	RW	10.0	7	97	0.14
	DW	10.0	7	121	0.25
	SW	5.0	7	92	0.14
	WW	5.0	7	91	0.50
	GW	10.0	7	96	0.35
	SD	2.0	7	98	0.08
o-Phosphate- P	RW	10.0	7	99	0.17
	DW	10.0	7	99	0.26
	SW	10.0	7	98	0.22
	WW	10.0	7	106	0.85
	GW	10.0	7	95	0.33
Sulfate	RW	20.0	7	99	0.40
	DW	50.0	7	105	3.35
	SW	40.0	7	95	1.7
	WW	40.0	7	102	6.4
	GW	40.0	7	112	3.2

RW = Reagent Water
DW = Drinking Water
SW = Surface Water
WW = Mixed Domestic and Industrial Wastewater
GW = Groundwater
SD = USEPA QC Solid (shale)

Table 2B. Single-Operator Accuracy and precision of By-Product (Part B)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromate	RW	5.0	7	103	0.07
		1.0	7	98	0.04
		0.1	7	155	0.005
		0.05	7	122	0.01
	DW	5.0	7	95	0.04
		1.0	7	85	0.02
		0.1	7	98	0.005
		0.05	7	98	0.005
Chlorate	RW	5.0	7	101	0.06
		1.0	7	97	0.01
		0.1	7	100	0.01
		0.05	7	119	0.05
	DW	5.0	7	101	0.04
		1.0	7	115	0.01
		0.1	7	121	0.005
		0.05	7	110	0.01
Chlorite	RW	5.0	7	100	0.04
		1.0	7	98	0.01
		0.1	7	86	0.01
		0.05	7	94	0.01
	DW	5.0	7	96	0.03
		1.0	7	100	0.02
		0.1	7	76	0.00
		0.05	7	96	0.01

RW = Reagent Water
DW = Drinking Water

PEAK NAME	RET TIME	CONC. in mg/L
Fluoride	1.17	2.0
Chloride	1.73	20.0
Nitrite	2.02	2.0
Bromide	2.95	2.0
Nitrate	3.20	10.0
	4.75	
Phosphate	5.38	2.0
Sulfate	6.92	60.0

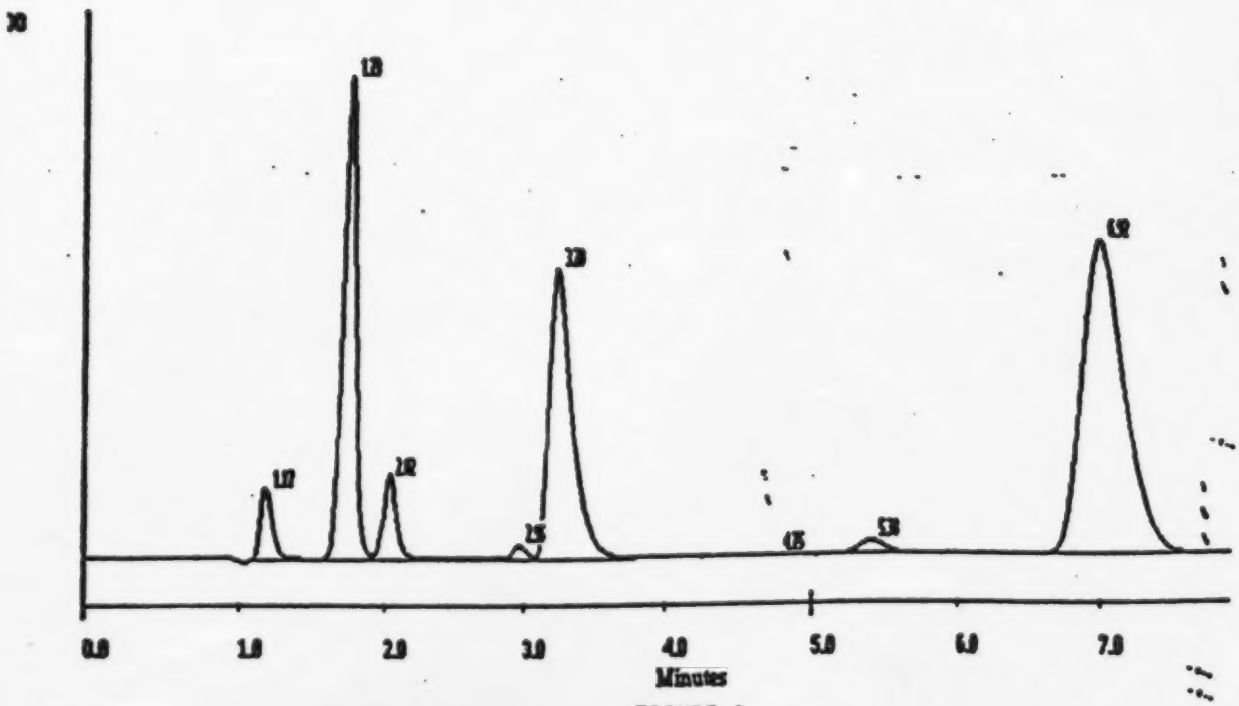

FIGURE 1
CHROMATOGRAM SHOWING SEPARATION USING THE AS4A COLUMN
(METHOD A)

PEAK NUMBER	RET TIME	PEAK NAME	CONC. in mg/L
	2.75	chLORITE	0.1
	3.23	BROMATE	0.1
	3.63	CHLORIDE	0.1
	7.08	CHLORATE	0.1

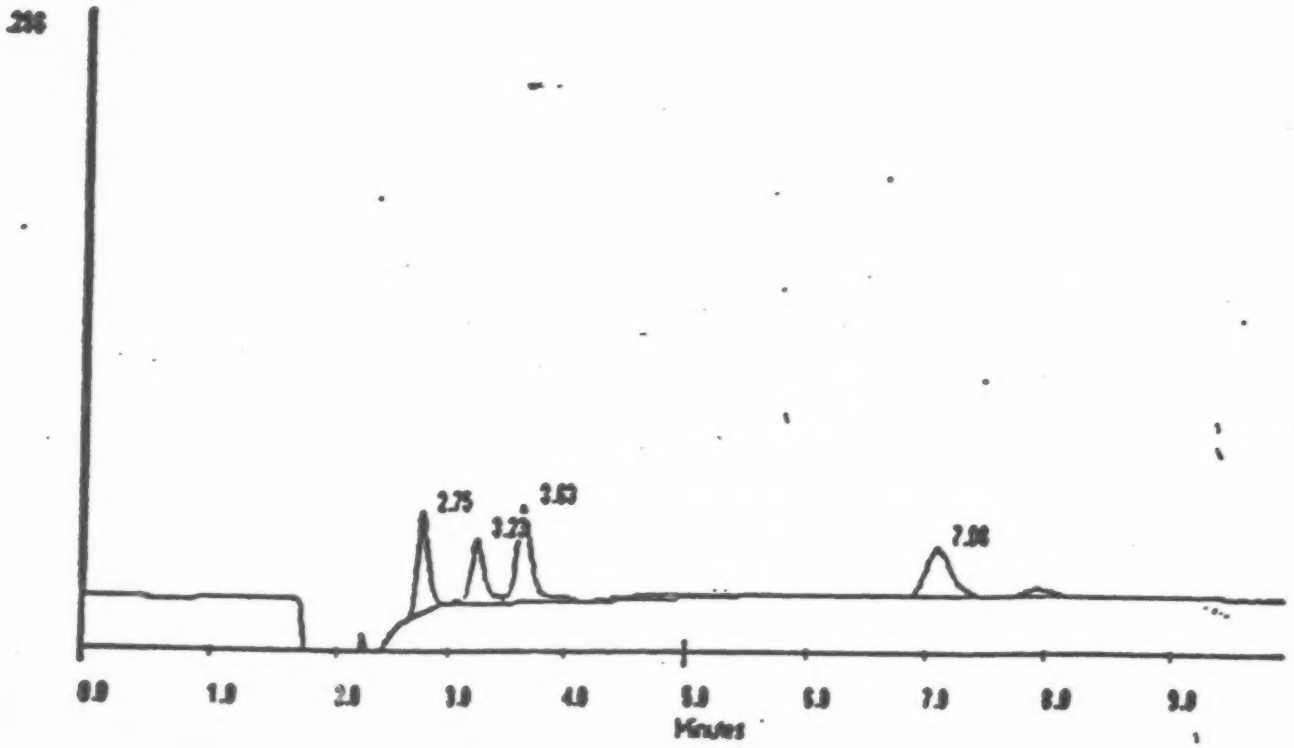

FIGURE 2

CHROMATOGRAM SHOWING SEPARATION USING THE AS9 COLUMN
(METHOD B)